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# ON SPECTRAL CHARACTERISTICS OF OZONISER DISCHARGE IN PURE NITROGEN AT 20 mm. PRESSURE

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Plates IV A, B

**ABSTRACT.** In the ozoniser discharge through nitrogen at 20 mm pressure are excited a large number of known band systems involving the following initial electronic levels, $D\,^3\Sigma_u^+$, $C\,^3\Pi_u$, $B\,^3\Pi_g$, $c_2\,^1\Sigma_u^+$, $m\,^1\Pi_u$, $l$, $s'\,^1\Sigma_u^+$, $h\,^1\Sigma_u^+$, $r'\,^1\Sigma_u^+$, $z$, $y(^1\Pi_g)$ and $x(^1\Sigma_g^-)$, with relative intensities visually estimated, ranging from 100 in the case of second positive to 0.5 for the first positive system of bands with 30 for the fourth positive and 20 for the singlet systems. Also, the first negative bands of $N_2^+$ are excited with intensity 60 in the above scale. Besides, there is evidence of three progressions of new bands which probably involve transitions from hitherto unknown electronic singlet levels to the $a\,^1\Pi_g$ state.

It is generally accepted that excitation of a molecule by electron collisions favours such excited states for which the inter-nuclear distance is not much different from that of the lower state while excitation by collisions with ions or atomic particles favours excited states which have greatly altered inter-nuclear distances. From this principle, the excitation of the $D\,^3\Sigma_u^+$ state ($r_e = 1.108$) and of $B\,^2\Sigma_u^+$ of the first negative bands of $N_2^+$ ($r_e = 1.075$) can be understood to be due to collisions of normal $N_2$ molecules with high speed electrons while that of the singlet electronic levels which involve a big change in the inter-nuclear distance (from 1.22 and 1.33 to 1.094, the $r_0$ in the ground state) is due to collisions with particles of atomic masses. The excitation of all these states simultaneously in the ozoniser discharge, indicates the significance of this type of discharge.

The abnormally low intensity of the first positive bands in this type of ozoniser discharge is attributed to deactivation of the initial electronic level $B\,^3\Pi_g$, due to collisions with atomic particles and a possible radiationless transfer to repulsive states.

## INTRODUCTION

The spectrum of an uncondensed discharge through nitrogen consists of the systems of the first and second positive bands which lie in the regions from the near infra-red to about 5000 Å and 4900 Å to 2820 Å respectively while the spectrum of a condensed discharge (Fowler and Strutt, 1911) contains in addition a single progression of the fourth positive system extending from 2900 Å to 2250 Å. But for this, the spectrum of nitrogen does not usually comprise of any strong systems in the quartz ultra-violet region. Recently, a number of weak band systems (Gaydon, 1944 ; Rosen and Herman, 1951 ; Herman, 1950 ; Janin, 1949, 1950 ; Janin and Crozet, 1948 ; Gaydon and Herman, 1946) have been discovered in this region of the spectrum under different conditions of excitation. In the course of the experiments of the spectroscopic studies of an ozoniser discharge through nitrogen (Appalanarasimaham, 1950-51) in relation to the Joshi effect, it was observed that the spectrum consists of the second positive system quite strong in intensity and the fourth positive system weaker than the second positive and in addition, a number of weak bands in the ultra-violet region many of which are identified with the new singlet systems, the fifth positive and the Kaplan's second systems. Besides these, three more groups of bands are obtained which could be arranged in progressions probably involving new electronic levels. In view of the development of almost all the systems of bands in the ozoniser discharge at comparatively high pressure of nitrogen, a detailed study of the spectrum has been made.

## EXPERIMENTAL PROCEDURE

The ozoniser used in the present experiments was originally prepared for the spectroscopic study of the Joshi effect in nitrogen. The ozoniser tube was filled with chemically pure and dry nitrogen at 20 mm pressure where the negative Joshi effect was found to be maximum at the 'threshold potential' (780 volts). The preparation of the tube has been described in detail in an earlier paper (Appalanarasimham, 1950-51). This ozoniser is excited in all the present studies by a transformer working off 110 volts A.C., 50 cycles primary and delivering about 6000 volts in the secondary. The spectrum is photographed on small and medium Hilger Quartz spectrographs. Kodak P 1200 Super Panchro Press and B 20 process regular plates have been used to photograph the respective spectra. Exposures of less than 4 hours were enough to record the more intense second positive bands on the medium instrument, whereas, the less intense bands in the ultra-violet needed exposures of 20 hours or more. The order of the intensities of the band systems of nitrogen obtained in the present experiments is roughly estimated visually and given in the following table with certain other relevant data. For this purpose a value of 100 is chosen for the intensity of the second positive system which is the most intense system and relative to it, the intensities of the other systems are estimated. Generally, the intense bands in any system are taken for the relative intensity estimation.

It was easy to identify directly from the spectrograms the bands obtained when these belonged to the well known second positive, first positive or fourth positive systems of nitrogen or to the negative bands of $N_2^+$. The wavelengths of the band heads of all other nitrogen bands were determined in the usual way by measuring the spectrograms and calculating the values from the Hartmann formula. The average discrepancy between the mean calculated values and the values given in literature was $\pm 0.5$ Å. The bands could thus be definitely identified with the known ones. The values given in literature are therefore employed in the discussion. In the course of the new classified and unclassified bands, the band head data obtained in the present experiments have been presented and used.

## OBSERVATIONS

(*a*) *Triplet systems of nitrogen.* The most intense of the triplet

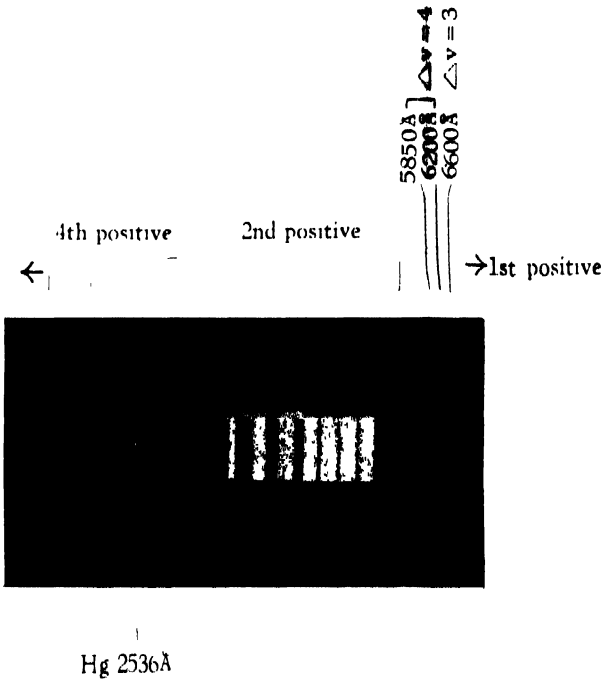
5850Å
6200Å
6600Å
$\Delta v = 4$
$\Delta v = 3$
4th positive
2nd positive
→1st positive
Hg 2536Å

Fig 1

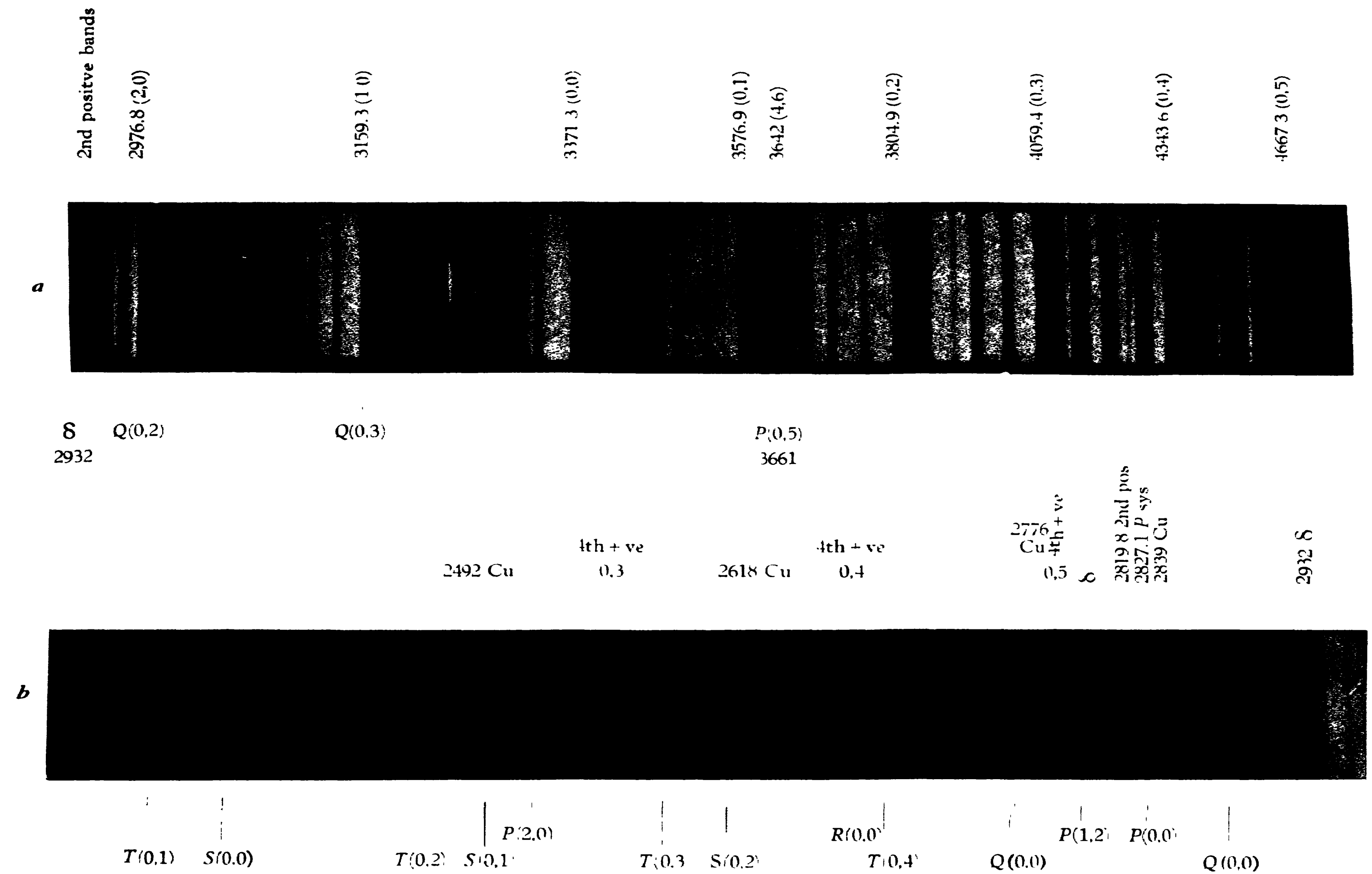
2nd positive bands
2976.8 (2,0)
3159.3 (1 0)
3371 3 (0,0)
3576.9 (0,1)
3642 (4,6)
3804.9 (0,2)
4059.4 (0,3)
4343 6 (0,4)
4667 3 (0,5)
a
δ 2932
Q(0,2)
Q(0,3)
P(0,5) 3661
2492 Cu
4th + ve 0,3
2618 Cu
4th + ve 0,4
2776 Cu
4th + ve 0,5
δ
2819 8 2nd pos
2827.1 P sys
2839 Cu
2932 δ
b
T(0,1)
S(0,0)
T(0,2)
S(0,1)
P(2,0)
T(0,3)
S(0,2)
R(0,0)
T(0,4)
Q(0,0)
P(1,2)
P(0,0)
Q(0,0)

Fig 2

systems of the nitrogen molecule is the second positive group. Long exposures of the ozoniser discharge bring out the fourth positive group and also very weak groups of bands belonging to the sequences $\Delta v = 3$ and 4 only of the first positive system (figure 1, Plate IV A).

The excitation of the fourth positive group (excitation potential ~ 12.6 e.v.) indicates that the mechanism of excitation approximates to the vigorous type as is generally met with in condensed discharges and is probably due to electrons of high velocity. Electronic collisions favour transitions to states in which the inter-nuclear distance does not suffer large changes. From this principle, the first negative, $N_2^+(r_e = 1.075)$ and the fourth positive $(r_e = 1.108)$ are to be regarded as being excited by electronic collisions in these experiments. The weak intensity of the first positive bands is probably a case of deactivation (Tawde and Patankar, 1947; Gaydon, 1944) of the initial level of the first positive system due to collisions and a possible radiationless transfer into a repulsive state.

(b) *Singlet systems of nitrogen.* In emission, eight systems of short progressions of bands are now known which have been obtained under different conditions of excitation by different authors, each of them obtaining some of these systems selectively depending upon the method of excitation employed. The discharge conditions under which the different band systems are excited are briefly as follows: Gaydon (1944) excited five of the band systems ($P$, $Q$, $R$, $S$, $T$ systems) in a hollow cathode discharge through a capillary tube of 2 mm bore and 20 cm long and the discharge was maintained by an ordinary induction coil with a small condenser and ½ inch spark gap. A flow of chemically dry and oxygen-free nitrogen was maintained in the discharge tube at a few mm pressure of mercurry. Mme. Renee Herman (1950) obtained the $P$, $\delta$ ($v'=0$, $v'=1$*), $S$, $T$, $\theta$, $\eta$ systems in an ordinary discharge at low pressures through a very long tube (25 m). Janin (1949, 1950) obtained the $P$, $\delta$ ($v=0$ and $v'=1$*) systems in an electrodeless discharge of the ozoniser type at low pressure of nitrogen while Janin and Crozet (1948) got the $\delta$ ($v'=0$ and $v'=1$*) systems in low pressure discharges in the presence of rare gases. Thus we see that there is a pronounced effect of the discharge conditions in bringing out the different systems. We shall now compare the systems excited in the present experiments with those described above. In every system only the recorded bands in the present experiments are given with the quantum numbers (figure 2, Plate IV B). These form the strongest bands in each system. The other bands of the systems are either absent or very weak.

1. *P system*: 2827 (0,0), 2967 (0,1), 3283 (0,3), 3661 (0,5)
   2785 (1,1), 2516 (2,0) and 2918 (1,2).

Of all the bands of the singlet systems excited in the present experiments the 2827 (0,0) band of this system is the strongest. This band is in fact

* This is the same as Gaydon's $Q$ progression.

stronger than the 2819 (3,0) band of the second positive system (see figure 2). Some of the bands of this system are superposed by the rotational lines of the second positive bands. Gaydon obtained only the (0,0), (0,1) and (0,2) bands of the progression $v'=0$ while Janin and Crozet (1948) obtained two more progressions viz., $v'=1$ and $v'=2$. In the present experiments only the stronger of these two progressions is obtained. However, the bands at 2662 (1,0) and 2871 (2,3) are not present on our plates though they are assigned intensity values of (10) and (6) by Janin and Crozet.

2. *Q system* : 2746 (0,0), 2878 (0,1), 3020 (0,2) and 3175 (0,3).

The (0,3) band at 3175 Å is not included by Gaydon (1944). All the four have been observed by Janin (1949, 1950) in the luminescence spectrum of a silent electric discharge at low pressure of nitrogen.

3. *δ system* : 2796 (0,0), 2932 (0,1), 3080 (0,2) and 3241 (0,3).

This progression and the *Q* progression were grouped into the same system by Gaydon and Herman (1946) who called it δ system. Janin (1949, 1950) also obtained both these progressions and tentatively put them into the same system. But Gaydon got only the *Q* system in his experiments of a mildly condensed discharge through a flowing stream of nitrogen through a capillary tube at low pressure. In a joint publication, Gaydon and Herman (1946) discussed this point and finally Gaydon put them as belonging to two systems in view of the incompatibility of the $\omega_1/_2$ (640 $cm^{-1}$) with the *B* value of about 1.36 obtained from a rotational analysis of the 2746 (0,0) band. In the present experiments, both these systems are recorded with almost equal intensity. In view of the rather widely differing discharge conditions, the excitation of the δ system of bands is probably characteristic of the ozoniser discharges of the type used by Janin and us, while it is not favoured in the hollow cathode discharges. The other sources favourable for the production of these bands are luminescence discharges and discharges in the presence of rare gases (Rosen and Herman, 1951).

In a compilation of the data of the nitrogen band systems made by Rosen and Herman (1951) which came to our hand rather late, Herman designates the 3080Å band of the δ system as the (1,2) band of a system whose origin is at 2841 Å. = 35188 $cm^{-1}$. This means that the above progression of the δ system is not the $v'=0$ progression but $v'=1$ progression. If this is true, there will be strong evidence for regarding the δ and *Q* as two different systems. A further point in favour of this view consists in the fact that Herman considers the two progressions $v'=0$ and $v'=1$ of the δ system are themselves the $v'=4$ and $v'=5$ progressions respectively of a system whose origin locates the 101456.0 $cm^{-1}$ electronic level found in absorption by Worley (1943).

4. *R system* : 2672 (0,0) and 2796 (0,1).

The (0,0) band at 2672Å is present while the band at 2796Å is rather crowded by two more bands viz., (0,5) of the *T* system and (0,0) of the system and as such its presence is not certain. It may be mentioned here that this system has been obtained only in a hollow cathode discharge by Gaydon. Further, Gaydon observed the band at 2672Å to be the most outstanding of the new bands. But on our plates the (0,0) band at 2827Å of the *P* system is probably the strongest of all the bands of the singlet systems.

5. *S and T systems :* *S* system : 2397 (0,0), 2497 (0,1), 2603 (0,2) and 2718 (0,3). *T* system : 2282 (0,0), 2372 (0,1), 2467 (0,2), 2570 (0,3) and 2796 (0,5).

Both these systems are equally strong on our plates, The (0,2) band of the *T* system was not observed earlier either by Gaydon or by Herman. This band is quite weak on our plates but it is clearly visible.

6. *θ System :* In addition to these bands, we find a weak structure of bands at 2358Å which is also the strongest band of the system of Herman. The other bands of the system are, however, not present.

*Other band systems of nitrogen :* Kaplan's second system . 2354 (0,0), 2537 (0,2), 2636 (0,4) and 2619 (1,4).

This system is rather weak and only the above bands are present on the plates. These bands are also the strongest bands of this system.

*Fifth positive (Van der Ziel's,) system :* 2412 (1,4), 2586 (1,6) and 2681 (1,7).

This system is the weakest of all the systems of bands described in these studies. The progression $v'=0$ is not observed at all. In fact, only the bands of the progression, $v'=1$, were observed originally by Van der Ziel, and later Gaydon and Herman (1946) observed a further weak progression which fitted into the $v'=0$ of this system.

*New band systems, probably singlet :* In addition to these systems, we got a number of other bands some of which are noticeable on Gaydon's published spectrograms (Gaydon, 1944) also. Eight of these could be arranged into three progressions as shown below.

| $v'$ \ $v''$ | 0 | | 1 | | 2 | | 3 |
|---|---|---|---|---|---|---|---|
| (*i*) 0 | λ 2462.3<br>ν 40600 | Δν<br>(1663) | 2567.5<br>38937 | Δν<br>(1631) | 2679.7<br>37306 | Δν<br>(1610) | 2810.6<br>35696 |
| (*ii*) 0 | λ 2723 *V*<br>ν 36713 | Δν<br>(1665) | 2852.4 *V*<br>35048 | | | | |
| (*iii*) 0 | λ 2839<br>ν 35213 | Δν<br>(1665) | 2980<br>33547 | | | | |

The vibrational wave number differences in the (*i*) system agree closely with those of the $a\,^1\Pi_u$ state viz., 1666, 1638, and 1610 $cm^{-1}$. These bands, therefore, locate a new level at 109557 $cm^{-1}$ of the $N_2$ molecule,

The progressions (*ii*) and (*iii*) are represented by only two bands each and are therefore less definite. It is, however, to be noted that Janin (1949) also recorded the bands of the (*iii*) progression. The band at 2839 Å is definitely present in Gaydon's spectrogram. The bands at 2980Å is likely to be missed in the structure of strong 2977Å band (2,0) of the second positive group. In our experiments the bands stand out clearly in a plate which records the 2977Å second positive band comparatively weakly, whereas, usually the band at 2980Å is masked by the structure of the strong second positive band at 2977Å.

The two bands at 2723 and 2852Å which are tentatively shown to form a new progression are not recorded by previous workers.

*Unclassified bands* :

The following bands are also present on our plates. 2417.9, 2424 0, 2459.6, 2612,0, 2673.0 and 2907,5 Some of these viz., 2424.0 and 2459.6 are present on Gaydon's plate.

## SUMMARY AND CONCLUSIONS

The prominent features of the spectrum excited in the ozoniser discharge through nitrogen at a pressure of 20 mm are the following .

(1). The first positive system is extremely weak while in the ordinary discharges the first positive system is comparable in intensity to the second positive system.

(2). The fourth positive system is excited. This system is usually excited only in condensed and other vigorous types of discharges through nitrogen.

(3). Seven systems out of the eight known singlet band systems are obtained in emission with the single mode of excitation employed, namely, ozoniser discharge through nitrogen at 20 mm. pressure. Previously these systems of bands have been excited under different excitation conditions like (*a*) the electrodeless discharge in the presence of rare gases (*b*) discharges through nitrogen at moderate but controlled pressures (*c*) hollow cathode discharge through nitrogen at low pressures.

(4). Other systems like the Kaplan's second system, the fifth positive system and several new bands for some of which a classification is proposed, are excited only weakly.

These features can be understood in the following way. It is generally known that the addition of a small amount of oxygen decreases the intensity of the first positive bands by deactivation (Tawde and Patankar, 1947 ; Gaydon, 1944) due to collisions with oxygen atoms. It is also likely that at high pressures collisions with particles of atomic masses may drift the molecules into a radiationless transition. In either case, collisions with atomic particles are essential. That this happens in the present ozoniser discharge through nitrogen is shown also by independent observations given below and elsewhere (Appalanasimham 1952-53). The second observation is indicative of the excitation of the nitrogen molecule to high energy states, the excitation energy of the fourth positive bands being 12.6 e.v. thus indicating the availability of high energy electrons in the ozoniser discharge. The third feature is significant. The molecule in these singlet states has an internuclear distance much larger (1.20 to 1,33) than in the ground state

TABLE I

| No. Band system | Transition | Sources favourable | $r_e$ in the initial state | Visually estimated intensity |
|---|---|---|---|---|
| *Triplet systems* : | | | | |
| 1. 2nd positive | $C^3\Pi_u \rightarrow B\,^3\Pi_g$ | Positive column discharges | 1.2123 | 100 |
| 2. 4th positive | $D\,^3\Sigma_u^+ \rightarrow B\,^3\Pi_g$ | Condensed discharges | 1.108 (*r*o) | 30 |
| 3. 1st positive | $B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+$ | Positive column discharges | 1.293 | 0.5 |
| *Singlet systems* : | | | | |
| 4. *P* systsm | $c_2\,^1\Sigma_u^+ \rightarrow a\,^1\Pi_g$ | Ozoniser discharges at low pressures | 1.12 (*r*o) | 40 |
| 5. *Q* ,, | $m\,^1\Pi_u \rightarrow a\,^1\Pi_g$ | Discharges at strong press., ozoniser discharges | 1.328 (*r*o) | 20 |
| 6. *δ* ,, | $1 \rightarrow a^1\Pi_g$ | Luminescence and ozoniser discharges: also in the presence of rare gases | (1.27) | ,, |
| 7. *R* ,, | $r'\,^1\Sigma_u^- \rightarrow a\,^1\Pi_g$ | Electrodeless discharges, medium pressures, mildly condensed discharges | 1.20 (*r*o) | ,, |
| 8. *S* ,, | $s'\,^1\Sigma_u^+ \rightarrow a\,^1\Pi_g$ | Electrodeless discharges, medium pressures, mildly condensed discharges | 1.232 (*r*o) | ,, |
| 9. *T* ,, | $h\,^1\Sigma_u^+ \rightarrow a\,^1\Pi_g$ | Moderate pressures, mildly condensed discharges | 1.22 (*r*o) | ,, |
| 10. Kalpan's 2nd systems | $y(^1\pi_g) \rightarrow w$ | Moderate pressures | 1.16 (*r*o) | 15 |
| 11. 5th positive or Van der Ziel's | $x(^1\Sigma_g^-) \rightarrow a'(^1\Sigma_u^-)$ | ,, ,, | 1.18 | 5 |
| 12a *θ* system | $z \rightarrow a\,^2\Pi_g$ | Strong current | — | |
| | | $\gamma_e$ of the grand state $x\,^1\Sigma_g^+$ | 1.094 | |

The spectrum also records two bands of $N_2^+$, first negative system, (0,0) and (0,1), with a visual intensity of 60 in scale employed.

In addition to the above, the following lines and band heads due to trace of impurities have been recorded on the long exposure plates, with intensities ranging from 10 to 20 on the above scale. 2883 Å and 2896 Å due probably to $CO_2^+$ 3064 Å due to OH and 2536 Å due to Hg

The designations of the electronic levels given in column 3 and the data of the $r_e$ and $r_e$ values and the sources favourable are taken from Rosen and Herman (1951).

($r_e = 1.094$). Electronic transitions involving relatively large changes in internuclear distance are known to be favoured either by atomic collisions or by discharges in the presence of rare gases. That in the ozoniser discharge employed almost all the singlet levels are excited is thus indicative of the appreciable availability for excitation, also of atomic collisions.

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